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INTRODUCTION AND RELATIONSHIP TO PREVIOUS WORK

The previous report of this series was concerned entirely with the photooxidative degradation of cellulose, catalyzed by ferric ion. Using the apparatus described, it was found that the presence of 0.1% ferric ion in a cellophane sheet had no appreciable catalytic effect on degradation when the treated sheet was exposed for five hours to radiation comprising wave lengths of 3600 to 7000 A. Since it had been shown previously (Final Summary Report on Contract CML-136, dated 28 February 1961) that as little as 0.004% ferric ion in a cotton fabric did accelerate photooxidative degration of the cotton under somewhat different conditions, it was expected that exposure times longer than five hours would produce degradation in the treated cellophane. The present report describes further studies of the photooxidative degradation of cellulose, catalyzed by ferric ion. Also included in the present report are quantitative measurements of the light intensities to which the treated cellulose has been exposed. These measurements were made with uranyl oxalate actinometers.

SUMMARY

Cellophane sheets were uniformly impregnated with ferric nitrate to ferric ion contents of 0.1% and 0.2%. Single sheets were exposed to radiation from a carbon arc, filtered to exclude light below 2900 A. and consisting primarily of light between 3500 and 5000 A. Untreated cellophane was used as the control. Exposures up to 15 hours produced no measurable loss in tensile strength for the treated or untreated sheets. A 36 hour exposure caused about 35% strength loss in the sheets containing 0.2% ferric ion, but no measurable strength loss in the untreated sheets or in those containing 0.1% ferric ion.

Swatches of cotton fabric were similarly impregnated with ferric nitrate and exposed. Untreated fabric was used as the control. In contrast to cellophane, the ferric ion impregnated cotton was significantly degraded by exposure times as short as ten hours. 36 hour exposure caused severe loss in the material containing 0.2% ferric ion, and some loss even in the untreated control. Thus it appears that cellophane may be more resistant than cotton to catalyzed photooxidative degradation, even though both are essentially cellulose. The current studies are being extended to explain this behavior.

An actinometer system based on uranyl oxalate was set up and calibrated. It was then used to measure the light intensities to which the above cellophane and cotton samples were exposed. For all of the exposures reported above the samples received about 7×10^{-8} moles of light energy per second per square centimeter. This value is about one-half of that for the same frequency range of bright sunlight,

FUTURE WORK PLANNED

1. The difference between cellophane and cotton, with regard to photooxidative degradation, will be studied. As part of this study the degree of degradation will be determined by cuprammonium fluidity measurements as well as by loss in tensile strength.

2. Degradation accelerators other than ferric ion will be studied. Those which can be conveyed to the textile substrate in vapor form, rather than as a solid or non-volatile liquid, are considered especially desirable.

3. Degradative methods for textile materials other than cellulose will be explored.

DETAILS

Exposures of Cellophane and Cotton Fabric Samples.

The cellophane used in these studies was the Avisco type 300,
described in the First Report of this series. Sheets were impregnated with
ferric nitrate by the technique previously described. Single sheets of the
cellophane, mounted on circular wooden hoops eight inches in diameter, were
exposed to radiation from the carbon arc of a Fadeometer at a distance of
50 cm. from the arc. The light was filtered by Corex windows to exclude
wave lengths below 2900 A. The radiation from the arc consisted mainly
of wave lengths from 3500 to 5000 A. In these experiments no attempt was
made to filter the UV radiation between 2900 and 3600 A or the IR radiation
above 7000 A. After a selected exposure time the sheets were removed from
the Fadeometer and conditioned at 70°F., 65% R.H. for at least 4 hours. One
by six inch strips were then die cut from the sheets (six inches in the machine
direction) and tested for breaking strength. For exposure times up to 15
hours, there was no apparent strength loss in the treated or untreated sheets,
or in unexposed controls. After 36 hours the cellophane containing 0.2%
ferric ion showed about 35% strength loss. There was no apparent strength
loss in the untreated control or in the cellophane containing 0.1% ferric
ion.

The cotton fabric used in these studies was bleached, 80 x 80 print-
cloth (Test Fabrics, Inc.) which has been used in previous degradation studies
(under contract CML-136). One by six inch die cut strips (six inches in warp
direction) of the untreated fabric, conditioned at 70°F., 65% R.H., had
breaking strengths of 54 ± 2 lbs. Swatches of the cotton fabric were impregnated
with ferric nitrate to ferric ion contents of 0.025%, 0.1%, and 0.2%. The
impregnations were carried out by applying the ferric nitrate solutions
dropwise to the fabric swatches so that they wicked evenly to the desired
add-ons. Mounted sheets of the treated and untreated fabrics or pre-cut six

by one inch strips were exposed to the carbon arc light source as were the cellophane sheets above. After exposure, one by six inch strips were die cut from the sheets and tested for breaking strength. No differences were observed between the strips cut before and after exposure. Exposures of 10 hours produced tensile strength losses of about 60% in the fabrics containing 0.1% and 0.2% ferric ion, but no measurable strength loss in the untreated fabric or the fabric containing 0.025% ferric ion. A 36 hour exposure caused about 10% strength loss in the untreated control, 20% strength loss in the fabric containing 0.025% ferric ion, and about 70% strength loss in the fabrics containing 0.1% and 0.2% ferric ion. The data are summarized in the accompanying Table.

The greater resistance of cellophane to photooxidative degradation, compared to the cotton fabric may possibly be due to differences in the amounts of light absorbed. This possibility is being checked.

Light Intensity Measurements.

The uranyl oxalate actinometer was made essentially as described by Leighton and Forbes (J. A. C. S. $\underline{52}$, 3139 (1930)). The overall actinometer reaction is: $2 H_2C_2O_4 + UO_2^{++} + h\nu = 2 H_2O + 2 CO + 2 CO_2 + UO_2^{++}$ with a quantum yield of 0.6 at wave lengths around 4000 A. The light-sensitive actinometer solution was prepared 0.01M in uranyl oxalate and 0.04M in oxalic acid. The uranyl oxalate was prepared in these laboratories according to the method of Forbes and Heidt (J. A. C. S. $\underline{56}$, 2363 (1934)). From its preparation through the subsequent boiling with excess ceric ion, the uranyl oxalate-oxalic acid solution was protected from light, except for the controlled exposure in the Fadeometer.

The procedure for measuring light intensity was as follows:

20.0 ml. of the actinometer solution was transferred to a Klett glass cell 5 cm. deep and 2.5 cm. in diameter. One of the plane glass windows of the cell was masked to leave exactly one square cm. open; the remainder of the cell was wrapped to exclude light. The cell was placed in the Fadeometer with the window at a distance of 50 cm. from the arc light source, and was exposed for a selected time interval. A 10.0 ml. aliquot was then transferred to a flask containing 10.0 ml. of 0.11M ceric sulfate in 2N sulfuric acid. The flask was heated just to the boil and then cooled to room temperature. The ceric ion in excess of that used in decomposing oxalate ion was titrated with 0.005M ferrous sulfate, using o-phenanthroline indicator for the end point.

From the relationship:

$$\frac{\text{moles oxalate destroyed}}{\text{moles light absorbed}} = 0.6,$$

the light absorbed by the actinometer was calculated. For the conditions described above, the light intensity was found to be 7×10^{-8} moles per second absorbed by the actinometer through the one square centimeter exposed area. If the light absorbed is assumed to have an average energy of $71,500$ calories per mole (the energy of light at 4000 A wave length), 7×10^{-8} moles per second is equivalent to about 4.5×10^{-3} calories per second.

TABLE 1.

DEGRADATIVE EFFECTS OF FERRIC ION
AND ACTINIC LIGHT ON CELLULOSE

Ferric ion applied as ferric nitrate from aqueous solution. Samples exposed in Fadeometer as described in text.

Substrate	% Ferric Ion in Sample	Exposure Time, Hours	Breaking Strength, lbs.[a]	% Loss in Breaking Strength[b]
Cellophane	0	0	14.1 ± 1.7	--
	0	36	13.5	0
	0.1	15	14.8	0
	0.1	36	13.4	0
	0.2	15	13.6	0
	0.2	36	9.3	34
Cotton Fabric	0	0	54 ± 2	--
	0	36	47	13
	0.025	10	52	0
	0.025	36	43	20
	0.1	10	19	65
	0.1	36	15	72
	0.2	10	19	65
	0.2	36	13	76

[a] One by six inch strips were broken. Cellophane cut six inches in machine direction; fabric cut six inches in warp direction. Values are averages for at least five strips. Control values are for 15, or more, strips.

[b] Based on untreated, unexposed control. Loss calculated as zero if average strength was within range for control.